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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER 22750/534

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 10/088241

INTERNATIONAL APPLICATION NO.

PCT/EP00/09042

INTERNATIONAL FILING DATE
(15.09.2000)
(16.09.1999)
15 September 2000

16 September 1999

TITLE OF INVENTION

## METHOD FOR PRODUCING A SYNTHETIC LEATHER

PPLICANT(S) FOR DO/EO/US ÖRDER, Kurt; GROITZSCH, Dieter and LORENZ, Horst				
oplicants herewith submit to the United States Designated/Elected Office (DO/EO/US) the following items and other information				
This is a FIRST submission of items concerning a filing under 35 U S.C. 371.				
This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371				
This express request to begin national examination procedures (35 U S C 371(f)) immediately rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).				
A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.				
A copy of the International Application as filed (35 U S C. 371(c)(2))				
a. 🔲 is transmitted herewith (required only if not transmitted by the International Bureau).				
b. 🗵 has been transmitted by the International Bureau.				
c.  is not required, as the application was filed in the United States Receiving Office (RO/US)				
A translation of the International Application into English (35 U.S.C. 371(c)(2)).				
Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C 371(c)(3))				
a. $\square$ are transmitted herewith (required only if not transmitted by the International Bureau).				
b.  have been transmitted by the International Bureau.				
c. A have not been made, however, the time limit for making such amendments has NOT expired				
d. 🖾 have not been made and will not be made.				
A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3))				
An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) (Unexecuted)				
A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).				
ems 11, to 16. below concern other document(s) or information included:				
1. 🖾 An Information Disclosure Statement under 37 CFR 1.97 and 1 98.				
2.  An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included				
3. 🖾 A FIRST preliminary amendment.				
A SECOND or SUBSEQUENT preliminary amendment.				
4. 🗵 A substitute specification.				
5. A change of power of attorney and/or address letter.				
6. 🗵 Other items or information. Marked-up version of the substitute specification; International Search Report together with An English				

translation; an English translation of the International Preliminary Examination Report and first page of the published International

EXPRESS MAIL NO.: EL327553805US

Application WO 01/20072.

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17. ☑ The following fee:	17. ⊠ The following fees are submitted.			CALCULATIONS	PTO USE ONLY
Basic National Fee (	(37 CFR 1.492(a)(1)-(5)):	; ;			
		or JPO			
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Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$1,040.00					
		to USPTO (37 CFR 1 482 2)-(4)			
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Claims	Number Filed	Number Extra	Rate		
Total Claims	17 - 20 =	0	X \$18.00	\$	
Independent Claims	1 - 3 =	0	X \$84.00	\$	
Multiple dependent claim(s)	(if applicable)		+ \$280.00		
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Reduction by ½ for filing by also be filed. (Note 37 CFF	small entity, if applicable ₹ 1.9, 1.27, 1.28).	· Verified Small Entity sta	tement must	\$	
SUBTOTAL =			\$ 890.00		
Processing fee of \$130.00 for furnishing the English translation later the 20 30 months from the earliest claimed priority date (37 CFR 1 492(f)) +			\$		
TOTAL NATIONAL FEE =			\$ 890.00		
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +			\$		
TOTAL FEES ENCLOSED =			\$ 890.00		
101/12/2002/			Amount to be: refunded	\$	
		****		charged	\$ 890.00
a. A check in the amount of \$ to cover the above fees is enclosed.					
b.   Please charge my Deposit Account No.   11-0600 in the amount of \$890.00 to cover the above fees. A duplicate copy of this sheet is enclosed					
c. 🖾 The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit  Account No11-0600 A duplicate copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1 494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status					
SEND ALL CORRESPONDENCE TO:					
SIGNATURE					
Kenyon & Kenyon					
One Broadway	One Broadway Richard M Rosati, Reg. No. 3			1,792	
New York, New York 10	1004	NAME			
15 March 2002					
	A.C.	DATE			

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PATENT TRADEMARK OFFICE

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[22750/534]

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Inventor(s)

Kurt JOERDER et al.

Serial No.

To Be Assigned

Filed

Herewith

For

METHOD FOR PRODUCING A SYNTHETIC LEATHER

Examiner

To Be Assigned

Art Unit

To Be Assigned

Assistant Commissioner for Patents Washington, D.C. 20231

# PRELIMINARY AMENDMENT AND 37 C.F.R. § 1.125 SUBSTITUTE SPECIFICATION STATEMENT

SIR:

Kindly amend the above-captioned application before examination, as set forth below.

## IN THE SPECIFICATION AND ABSTRACT:

In accordance with 37 C.F.R. § 1.121(b)(3), a Substitute Specification (including the Abstract, but without claims) accompanies this response. It is respectfully requested that the Substitute Specification (including Abstract) be entered to replace the Specification of record.

## IN THE CLAIMS:

On the first page of the claims, first line, change "What is claimed is:" to --WHAT IS CLAIMED IS:--.

Please cancel, without prejudice, claims 1 to 10 in the underlying PCT application.

Please add the following new claims:

--11. (New) A method for producing a synthetic leather that includes a nonwoven fabric that contains microfibers, comprising the steps of:

processing thermoplastic microfibers having a titer of 0.05 to 1.0 dtex and fibers soluble in hot water having a titer of 4 to 6 dtex in a weight ratio of 90:10 to 30:70 to form a nonwoven fabric having a surface weight of 80 to 1,000 g/m<sup>2</sup>;

applying and consolidating an aqueous polymer dispersion of a viscoelastic substance in a weight ratio of 25:75 to 75:25 of the nonwoven fabric to the viscoelastic substance; and

subsequently extracting the fibers soluble in hot water.

- 12. (New) The method according to claim 11, wherein the titer of the thermoplastic microfibers is 0.1 to 0.3 dtex, the weight ratio of the microfibers to the fibers soluble in hot water is 70:30 to 50:50 wt.-%, the surface weight of the nonwoven fabric is 100 to 500 g/m², and the ratio of the nonwoven fabric to the viscoelastic substance before the extracting step is 35:65 to 65:35 wt.-%.
- 13. (New) The method according to claim 11, wherein the thermoplastic microfibers include split fibers.
- 14. (New) The method according to claim 12, wherein the thermoplastic microfibers include split fibers.
- 15. (New) The method according to claim 13, wherein the split fibers include one of polyethylene terephthalate/polyamide 6, polyethylene terephthalate/polyamide 6.6, polyethylene terephthalate/polyethylene, and polyethylene terephthalate/polyethylene.
- 16. (New) The method according to claim 14, wherein the split fibers include one of polyethylene terephthalate/polyamide 6, polyethylene terephthalate/polyamide 6.6, polyethylene terephthalate/polyethylene, and polyethylene terephthalate/polyethylene.

- 17. (New) The method according to claim 11, wherein the fibers soluble in hot water include fibers made of one of polyvinyl alcohol, poly-ε-caprolactone, carboxymethyl cellulose and starch.
- 18. (New) The method according to claim 12, wherein the fibers soluble in hot water include fibers made of one of polyvinyl alcohol, poly-ε-caprolactone, carboxymethyl cellulose and starch.
- 19. (New) The method according to claim 11, wherein further comprising the step of consolidating and splitting the nonwoven fabric using a high-pressure water jet.
- 20. (New) The method according to claim 11, wherein the aqueous polymer dispersion includes one of polyurethane, nitrile-butadiene rubber and styrene-butadiene rubber as a binder.
- 21. (New) The method according to claim 13, further comprising the step of adding a filler to the thermoplastic microfibers.
- 22. (New) The method according to claim 21, wherein the filler includes at least one of a pigment, a hydrophobization agent, a hydrophilization agent, an agent configured to reduce wettability with alcohols, fats and oils, an anti-static agent and an antimicrobial substance.
- 23. (New) The method according to claim 11, further comprising a subsequent treatment step, the subsequent treatment step including one of buffing, grinding and polishing with emery.
- 24. (New) The method according to claim 11, wherein the extracting step includes the substep of dissolving out the fibers soluble in hot water at a same time with exhaust dyeing.
- 25. (New) The method according to claim 24, wherein the exhaust dyeing is performed in an autoclave.

- 26. (New) The method according to claim 14, further comprising the step of adding a filler to the thermoplastic microfibers.
- 27. (New) The method according to claim 26, wherein the filler includes at least one of a pigment, a hydrophobization agent, a hydrophilization agent, an agent configured to reduce wettability with alcohols, fats and oils, an anti-static agent and an antimicrobial substance.—.

## REMARKS

This Preliminary Amendment cancels, without prejudice, claims 1 to 10 in the underlying PCT Application No. PCT/EP00/09042 and adds new claims 11 to 27. The new claims, <u>inter alia</u>, conform the claims to U.S. Patent and Trademark Office rules and do not add any new matter to the application.

In accordance with 37 C.F.R. § 1.121(b)(3), the Substitute Specification (including the Abstract, but without the claims) contains no new matter. The amendments reflected in the Substitute Specification (including Abstract) are to conform the Specification and Abstract to U.S. Patent and Trademark Office rules or to correct informalities. As required by 37 C.F.R. §§ 1.121(b)(3)(iii) and 1.125(b)(2), a Marked-Up Version of the Substitute Specification comparing the Specification of record and the Substitute Specification also accompanies this Preliminary Amendment. Approval and entry of the Substitute Specification (including Abstract) is respectfully requested.

The underlying PCT Application No. PCT/EP00/09042 includes an International Search Report, dated January 29, 2001, a copy of which is included. The Search Report includes a list of documents that were considered by the Examiner in the underlying PCT application.

The underlying PCT Application No. PCT/EP00/09042 also includes an International Preliminary Examination Report, dated December 6, 2001. An English translation of the International Preliminary Examination Report is included herewith.

It is respectfully submitted that the subject matter of the present application is new, non-obvious and useful. Prompt consideration and allowance of the application are respectfully requested.

Respectfully submitted,

**KENYON & KENYON** 

Dated: Mark 15, 200

Ву:

Richard M. Rosati Reg. No. 31,792

One Broadway New York, New York 10004 (212) 425-7200

[22750/534]

## METHOD FOR PRODUCING A SYNTHETIC LEATHER

## FIELD OF THE INVENTION

The invention relates to a method for producing a synthetic leather made up of a nonwoven fabric that contains microfibers.

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## BACKGROUND INFORMATION

Synthetic leathers based on nonwoven fabrics may be built up almost exclusively of microfibers. It has been shown that homogeneous microfibers as such cannot be processed on carding machines, or can be processed only at unjustifiable, extremely low production speeds. Therefore multi-component fibers such as matrix-fibril fibers or island-in-sea type fibers are used, or others with a different distribution of the two-fiber components, with a fiber titer such that they can be carded without loss of speed. The cross-sections of such fibers have an orange structure or a pie structure or hollow pie structure, for example. Such multi-component fibers (conjugate fibers, multiconstituent fibers) can be made up of at least two, but also up to approximately 18 segments. individual fiber segments of the usually two polymers alternate with one another, so that after each segment, fiber border surfaces, such as polyethylene terephthalate/polyamide 6, are formed. The separation of these multi-component fibers to yield isolated, ultrafine microfibers is done using different methods. For example, one of the two fiber components is dissolved out, using organic solvents, so that the other fiber component, which is insoluble in the organic solvent, remains behind as a microfiber. This method is complicated, not good for the environment, and connected with a high level of material loss as well as the accumulation of solvent that contains polymer, where treatment of the used solvent occurs either by solvent recycling or energy utilization.

SUBSTITUTE SPECIFICATION

NY01 457926 v 1

An environmentally friendly separation of the bi-component fibers occurs by splitting the fibers using high-pressure The bi-component split fibers are either composed water jets. of thermoplastics that are greatly different in terms of their chemistry, which do not possess any high adhesion forces bonding them to one another at their border surfaces, or which have been mixed with dehesive additives, i.e., additives that reduce the adhesion forces, if the fiber polymers are similar. A synthetic leather with a soft feel is described in Japanese Published Patent Application No. 5-78986, which contains a nonwoven fabric layer of melt-blown polyethylene terephthalate microfibers with a diameter of 0.1 to 0.6  $\mu m$  on at least one side. The softness is achieved in that the nonwoven fabric is coated with a dressing of polyvinyl alcohol that is soluble in cold water, before being impregnated with polyurethane from organic solvents such as dimethyl formamide. impregnation and coagulation of the polyurethane solution with water (so-called migration method), and the subsequent wash cycles for the purpose of removing the organic solvent, the polyvinyl alcohol is removed from the nonwoven fabric again, at the same time. Subsequent treatment of the synthetic leather obtained occurs in a conventional manner, by grinding, dyeing, and brushing. U.S. Patent No. 4,390,566 describes the production of a synthetic leather in which split microfibers are used, among other things. The microfiber nonwoven fabric is impregnated with a water-soluble dressing solution that is referred to as a temporary filler, before the binder is applied, and after the binder application has consolidated, this solution is washed out again. Polyvinyl alcohol (PVA), poly-s-caprolactone, carboxymethyl cellulose (CMC) or starch are used as temporary water-soluble fillers.

It is an object of the present invention to provide a process that permits the production of a very soft synthetic leather with improved properties. Another object of the present invention is to make production more cost-effective and better for the environment.

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#### SUMMARY

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The above and other beneficial objects are achieved, according to the present invention, by a process in which thermoplastic microfibers with a titer of 0.05 to 1.0 dtex and fibers soluble in hot water, with a titer of 4 to 6 dtex, are processed, in a weight ratio of 90:10 to 30:70, to form a nonwoven fabric with a surface weight of 80 to 1,000 g/m², and an aqueous polymer dispersion of a viscoelastic substance is applied and consolidated in a weight ratio of 25:75 to 75:25 of the nonwoven fabric to the viscoelastic substance, where subsequently extraction of the fibers soluble in hot water occurs.

The process according to the present invention may be one in which the titer of the thermoplastic fibers is 0.1 to 0.3 dtex, the weight ratio of the microfibers to the fibers soluble in hot water is 70:30 to 50:50 wt.-%, the surface weight of the nonwoven fabric is 100 to 500 g/m², and the ratio of the nonwoven fabric to the viscoelastic substance before removal of the fibers that are soluble in hot water is 35:65 to 65:35 wt.-%.

In the process according to the present invention, the thermoplastic fibers may include split fibers.

Furthermore, the split fibers may include polyethylene terephthalate/polyamide 6, polyethylene terephthalate/polyamide 6.6, polyethylene terephthalate/polypropylene, or polyethylene terephthalate/polyethylene.

Fibers that are soluble in hot water that are made of polyvinyl alcohol, poly- $\epsilon$ -caprolactone, carboxymethyl cellulose, or starch, may be used in the process according to the present invention.

Consolidation and splitting of the nonwoven fabric of fibers may occur using high-pressure water jets.

Furthermore, an aqueous polymer dispersion of polyurethane, nitrile-butadiene rubber, or styrene-butadiene rubber may be used as the binder.

It may be provided, according to the process according to the present invention, that fillers such as pigments,

hydrophobization or hydrophilization agents, agents to reduce wettability with alcohols, fats and oils, anti-static agents and/or antimicrobial substances may be added to the thermoplastic fibers.

Subsequent treatment may occur by buffing, grinding, or polishing with emery.

Dissolving out the fibers that are soluble in hot water may occur at the same time with exhaust dyeing, e.g., in an autoclave.

The process according to the present invention is not only simple, i.e., it makes do with only a few process steps, it also, at the same time, permits more cost-effective and environmentally friendly production of the synthetic leather.

Using the process according to the present invention, there may be no need to use organic solvents to release the microfibers, or to apply the binder coagulation.

## DETAILED DESCRIPTION

The production of a synthetic leather, according to the present invention, occurs in that a fiber sheet is produced from endless fibers, staple fibers, or short-cut fibers, using the conventional fiber laying techniques. This fiber sheet is made up of at least two fiber components, where at least one of the fiber components is a bi-component fiber that may be

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split using high-pressure water jets. Such split fibers are made up of at least two thermoplastic polymer components, P1 and P2, which are arranged in segments around the fiber axis, in alternating sequence. In this connection, both centric and eccentric fiber axis arrangements are possible. The number of segments is between 2 and 30, e.g., between 4 and 24. total titer of these so-called pie fibers is between 0.8 and 5.0, e.g., between 1.0 and 3.3 dtex. According to the present invention, other geometric arrangements of the fiber polymers P1 and P2 are also possible, with the proviso that the fibers are split up into microfibers by at least 80% under strong mechanical or hydrodynamic forces, such as treatment with high-pressure water jets. The polymer pairs P1 and P2 may include ones in which common border surfaces may not exert any strong adhesion forces on one another. Conventional P1/P2 pairs include, for example, polyethylene terephthalate/polyamide 6, polyethylene terephthalate/polyamide 6.6, polyethylene terephthalate/polypropylene, and polyethylene terephthalate/polyethylene. For P1/P2 pairs that are closely related in terms of chemistry, such as polypropylene and polyethylene or their copolymers, it is conventional to provide them with parting agents at their border surfaces, which ensure splittability. Also, metallocene-catalyzed polyolefins may be used as the polymer component P1 and/or P2. The fiber polymer components P1 and P2 may be spin-dyed, white-pigmented, or provided with agents that give the fiber polymer components hydrophilic or hydrophobic properties or reduced wettability with alcohol, other organic fluids, fats, or oils. Furthermore, the fiber polymer components may be mixed with anti-static agents or antimicrobial substances.

According to the present invention, in addition to the split fibers, at least a second fiber component is also used, which is composed in part or by 100% of a polymer soluble in hot water, where the portion of the nonwoven fabric soluble in hot water is 10 to 70 wt.-%. In the sense of the invention,

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solubility of the fibers in hot water is understood to mean a solubility in water under the conditions of high-pressure water jet treatment of less than 5%, and a solubility of at least 95% in water with a temperature of approximately 98 °C, i.e., in pressure containers at temperatures above 100 °C. Fibers soluble in hot water, in the sense of the invention, are also fibers that do not go into solution until they are treated with pressure in an autoclave, or swell up under these conditions to such an extent that they are removed by at least 95% from the nonwoven fabric when subjected to a washing procedure. Fibers that are soluble in hot water may include fibers made of polyvinyl alcohol or poly-ɛ-caprolactone.

The nonwoven fabric may contain other fibers, in addition to the splittable fibers and the fibers soluble in hot water, but nonwoven fibers made of the two fiber types stated are possible. The weight ratio of the split fibers and fibers soluble in hot water is 90:10 to 30:70, e.g., 70:30 to 50:50.

The fiber soluble in hot water may be present in weakly crosslinked form. Also, fibers that possess only a coating of a polymer soluble in hot water, i.e., fibers that have a coremantle structure, may be used as the fibers soluble in hot Furthermore, fibers with a side-by-side structure that are made up of different polymers, only one of which is soluble in hot water, are suitable. According to the present invention, the split fiber does not possess any coating that is soluble in hot water. Introduction of the fibers soluble in hot water occurs statistically in accordance with their proportion, for example by carding or the air-laid process or deposition on a slanted screen in accordance with the Fourdrinier method. In the case of split fiber endless filaments, fibers that are soluble in hot water are blown in at the side, using an air stream, into the endless filaments that exit from the spinning dies and are quenched and stretched by a directed air stream before being deposited on a screen belt, or the addition occurs from a separate spinning

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The split fibers and fibers soluble in hot water that are used may have a wavy structure. The fibers deposited to form a nonwoven sheet are transferred to a water removal screen and subjected to high-pressure water-jet treatment. a first stage, the fibers are merely intertwined, using a low water-jet pressure, to form a nonwoven fabric highly resistant to tearing. Subsequently, splitting of the split fibers to form microfibers with a titer between 0.05 to 1.0 dtex, e.g., 0.1 to 0.3 dtex, occurs using one or more high-pressure water-The fineness of the released microfibers may be iet beams. adjusted by the titer of the split fibers in the unsplit state and the number of segments. To prevent water-jet alleys in the nonwoven fabric, at least the last water-jet beams are put into oscillating motion perpendicular to the machine transport direction. Furthermore, to reduce alley formation, screens with a closer mesh may be used, which cause reflection and scattering of the incident water jets, and thereby cause the water-jet alleys to be made less distinct. Nonwoven fabrics with a surface weight of 80 to 1,000  $g/m^2$ , e.g., 100 to 500  $g/m^2$ , are produced using the process according to the present The nonwoven fabric may be mechanically needleinvention. punched, in addition, before the hydrodynamic treatment. process according to the present invention is conducted so that after splitting to form microfibers, a maximum of 3 to 5 wt.-% of the fibers soluble in hot water is dissolved out of the nonwoven fabric by the water-jet needle-punching and splitting process. The consolidated nonwoven fabric that is obtained is impregnated, in a conventional manner, with an aqueous binder dispersion, using the dry-in-wet application The application may occur by brushing, slop padding from one side, or full-bath impregnation in a Foulard. Application of the binder to one side may be promoted by applying a vacuum on the opposite side of the nonwoven fabric. The binder application occurs at a ratio of 25:75 to 75:25 wt.-%, e.q., 35:65 to 65:35 wt.-%, in relation to the prefinished nonwoven fiber fabric, i.e., before the fibers soluble in hot water are dissolved out. Polymers that contain

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self-cross-linking reactive groups in the polymer, or polymers mixed with cross-linking agents, are used as binders. selection of the polymer dispersions and cross-linking agents, care may be taken to ensure that the reactive groups in the 5 fibers soluble in hot water either remain non-cross-linked or that the degree of cross-linking is kept so low that the water solubility is retained, to remove the portion according to the present invention. Binders that are used in the sense of the invention are polymer dispersions made of polyurethane, nitrile-butadiene rubber and/or styrene-butadiene rubber. 10 Binders that smear when buffed or ground with sandpaper or on ceramic rollers are not binders in the sense of the invention. The binder may include conventional substances, such as inorganic white pigments, colored pigments, agents to improve the feel, such as silicones, cellulose dust, optical 15 brighteners, anti-static agents, bacteriostatics added to After the binder application, the nonwoven fabric is dried. If necessary, this is preceded by thermocoagulation and cross-linking or vulcanization. Subsequently, the synthetic leather obtained may be buffed and pre-ground. 20 Removal of the fibers soluble in hot water occurs either without pressure, under hot-water washing conditions, or in an autoclave, at bath temperatures above 100 °C. In this manenr, the fiber soluble in hot water is removed from the microfiber nonwoven fabric. Dissolving out the fiber soluble in hot 25 water may also be combined with an exhaust-dyeing process, if high dyeing temperatures are being used in any case, e.g., in an autoclave. Using the process according to the present invention, synthetic leathers that are extremely soft and firm, with excellent haptic properties, are obtained. 30 improve the microfiber nap, additional subsequent treatment steps, such as application of a finish to improve the feel, or fine-grinding of the surfaces, may occur.

## 35 Example

A fiber layer is produced from 80 parts by weight of a polyester-polyamide split fiber with a titer of 2.2 dtex and a

fiber length of 51 mm as well as 20 parts by weight of a polyvinyl alcohol fiber with a titer of 1.4 dtex and a fiber length of 38 mm, and this layer is needle-punched intensively to consolidate it. The nonwoven fabric obtained in this manner is subjected to high-pressure water-jet treatment, during which approximately 90 % of the polyester-polyamide fibers are split into microfibers. Subsequently, the nonwoven fabric is impregnated with a binder, where this is composed of aqueous dispersions that contain 70 parts by weight polyurethane, 20 parts by weight polyvinyl alcohol, 5 parts by weight colored pigments, as well as fillers and agents to improve the feel as solid components, for the remainder. After the impregnated nonwoven fabric is dried, the polyvinyl alcohol fibers are removed from the nonwoven fabric by more than 95 wt.-% by treatment in a hot-water washing cycle. synthetic leather obtained has a very round feel and may be processed to produce a material with a nubuck appearance by subsequent grinding.

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## ABSTRACT

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A method is for producing a synthetic leather made up of a nonwoven fabric that contains microfibers. Production occurs in that thermoplastic microfibers with a titer of 0.05 to 1.0 dtex and fibers soluble in hot water, with a titer of 4 to 6 dtex, are processed, in a weight ratio of 90:10 to 30:70, to form a nonwoven fabric with a surface weight of 80 to 1,000 g/m², and impregnated with an aqueous polymer dispersion of a viscoelastic substance in a weight ratio of 25:75 to 75:25 of the nonwoven fabric to the viscoelastic substance, fixation of the viscoelastic substance occurs by cross-linking or vulcanization, and subsequently the fibers soluble in hot water are extracted from the nonwoven fabric.

[22750/534]

#### METHOD FOR PRODUCING A SYNTHETIC LEATHER

[Specification

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#### | FIELD OF THE INVENTION

The invention relates to a method for producing a synthetic leather made up of a nonwoven fabric that contains microfibers.

## BACKGROUND INFORMATION

Synthetic leathers based on nonwoven fabrics [are] may be built up almost exclusively of microfibers [at present]. has been shown that homogeneous microfibers as such cannot be processed on carding machines, or can be processed only at unjustifiable, extremely low production speeds. Therefore [preferably] multi-component fibers such as matrix-fibril fibers or island-in-sea type fibers are used, or others with a different distribution of the [preferably] two-fiber components, with a fiber titer such that they can be carded The cross-sections of such fibers have without loss of speed. an orange structure or a pie structure or hollow pie structure, for example. Such multi-component fibers (conjugate fibers, multiconstituent fibers) can be made up of at least two, but [preferably] also up to approximately 18 The individual fiber segments of the usually two polymers alternate with one another, so that after each segment, fiber border surfaces, such as polyethylene terephthalate/polyamide 6, are formed. The separation of these multi-component fibers to yield isolated, ultrafine microfibers is done using different methods. For example, one of the two fiber components is dissolved out, using organic solvents, so that the other fiber component, which is insoluble in the organic solvent, remains behind as a microfiber. This method is complicated, not good for the environment, and connected with a high level of material loss

as well as the accumulation of solvent that contains polymer, where treatment of the used solvent [takes place] <u>occurs</u> either by solvent recycling or energy utilization.

An environmentally friendly separation of the bi-component fibers[, which is preferred at present, takes place] occurs by splitting the fibers using high-pressure water jets. bi-component split fibers are either composed of thermoplastics that are greatly different in terms of their chemistry, which do not possess any high adhesion forces bonding them to one another at their border surfaces, or which have been mixed with dehesive additives, i.e., additives that reduce the adhesion forces, if the fiber polymers are similar. A synthetic leather with a soft feel is [known from the document JP 05078986] described in Japanese Published Patent Application No. 5-78986, which contains a nonwoven fabric layer of melt-blown polyethylene terephthalate microfibers with a diameter of 0.1 to 0.6  $\mu m$  on at least one side. softness is achieved in that the nonwoven fabric is coated with a dressing of polyvinyl alcohol that is soluble in cold water, before being impregnated with polyurethane from organic solvents such as dimethyl formamide. After impregnation and coagulation of the polyurethane solution with water (so-called migration method), and the subsequent wash cycles for the purpose of removing the organic solvent, the polyvinyl alcohol is removed from the nonwoven fabric again, at the same time. Subsequent treatment of the synthetic leather obtained [takes place in known] occurs in a conventional manner, by grinding, dyeing, and brushing. [Document US-A] U.S. Patent No. 4,390,566 describes the production of a synthetic leather in which split microfibers are used, among other things. microfiber nonwoven fabric is impregnated with a water-soluble dressing solution that is referred to as a temporary filler, before the binder is applied, and after the binder application has consolidated, this solution is washed out again. Polyvinyl alcohol (PVA), poly-ε-caprolactone, carboxymethyl

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cellulose (CMC) or starch are used as temporary water-soluble fillers.

[The invention has set itself the task of indicating] It is an object of the present invention to provide a process that permits the production of a very soft synthetic leather with improved properties. Another [task] object of the present invention is to make production more cost-effective and better for the environment.

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#### SUMMARY

The above and other beneficial objects are achieved [This task is accomplished], according to the present invention, by a process in which thermoplastic microfibers with a titer of 0.05 to 1.0 dtex and fibers soluble in hot water, with a titer of 4 to 6 dtex, are processed, in a weight ratio of 90:10 to 30:70, to form a nonwoven fabric with a surface weight of 80 to 1,000 g/m², and an aqueous polymer dispersion of a viscoelastic substance is applied and consolidated in a weight ratio of 25:75 to 75:25 of the nonwoven fabric to the viscoelastic substance, where subsequently extraction of the fibers soluble in hot water [takes place.] occurs.

[Preferably, the] <u>The</u> process according to the present invention [is] <u>may be</u> one in which the titer of the thermoplastic fibers is 0.1 to 0.3 dtex, the weight ratio of the microfibers to the fibers soluble in hot water is 70:30 to 50:50 wt.-%, the surface weight of the nonwoven fabric is 100 to 500 g/m², and the ratio of the nonwoven fabric to the viscoelastic substance before removal of the fibers that are soluble in hot water is 35:65 to 65:35 wt.-%.

[It is especially preferred according to] <u>In</u> the process according to the present invention [that], the thermoplastic fibers [are] <u>may include</u> split fibers.

Furthermore, [it is preferred that] the split fibers [are composed of] may include polyethylene terephthalate/polyamide 6, polyethylene terephthalate/polyamide 6.6, polyethylene terephthalate/polypropylene, or polyethylene terephthalate/polyethylene.

[Preferably, fibers] <u>Fibers</u> that are soluble in hot water that are made of polyvinyl alcohol, poly-\varepsilon-caprolactone, carboxymethyl cellulose, or starch, [are] <u>may be</u> used in the process according to the present invention.

Consolidation and splitting of the nonwoven fabric of fibers [preferably takes place] <u>may occur</u> using high-pressure water jets.

Furthermore, [it is preferred that] an aqueous polymer dispersion of polyurethane, nitrile-butadiene rubber, or styrene-butadiene rubber [is] <u>may be</u> used as the binder.

[Preferably it is] It may be provided, according to the process according to the present invention, that fillers such as pigments, hydrophobization or hydrophilization agents, agents to reduce wettability with alcohols, fats and oils, anti-static agents and/or antimicrobial substances [are] may be added to the thermoplastic fibers.

[In an advantageous further development of the process, it is provided that subsequent treatment takes place] <u>Subsequent</u> <u>treatment may occur</u> by buffing, grinding, or polishing with emery.

[It is especially preferred according to the process according to the present invention that dissolving] <u>Dissolving</u> out the fibers that are soluble in hot water [takes place] <u>may occur</u>

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at the same time with exhaust dyeing, [particularly] <u>e.g.</u>, in an autoclave.

The process according to the present invention is not only simple, i.e., it makes do with only a few process steps, it also, at the same time, permits more cost-effective and environmentally friendly production of the synthetic leather.

Using the process according to the present invention, there [is] <u>may be</u> no need to use organic solvents to release the microfibers, or to apply the binder coagulation.

## **DETAILED DESCRIPTION**

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The production of a synthetic leather, according to the present invention, [takes place] occurs in that a fiber sheet is produced from endless fibers, staple fibers, or short-cut fibers, using the [known] conventional fiber laying This fiber sheet is made up of at least two fiber techniques. components, where at least one of the fiber components is a bi-component fiber that [can] may be split using high-pressure water jets. Such split fibers are made up of at least two thermoplastic polymer components, P1 and P2, which are arranged in segments around the fiber axis, in alternating sequence. In this connection, both centric and eccentric fiber axis arrangements are possible. The number of segments [lies] is between 2 and 30, [preferably, however] e.g., between 4 and 24. The total titer of these so-called pie fibers [lies] is between 0.8 and 5.0, [preferably] e.g., between 1.0 and 3.3 dtex. According to the present invention, other geometric arrangements of the fiber polymers P1 and P2 are also possible, with the proviso that the fibers are split up into microfibers by at least 80% under strong mechanical or hydrodynamic forces, such as treatment with high-pressure water jets. [Preferably, the] The polymer pairs P1 and P2 [are] may include ones [whose] in which common border surfaces

[do] may not exert any strong adhesion forces on one another. [Known] Conventional P1/P2 pairs [are] include, for example, polyethylene terephthalate/polyamide 6, polyethylene terephthalate/polyamide 6.6, polyethylene terephthalate/polypropylene, and polyethylene 5 terephthalate/polyethylene. For P1/P2 pairs that are closely related in terms of chemistry, such as polypropylene and polyethylene or their copolymers, it is [known] conventional to provide them with parting agents at their border surfaces, which ensure splittability. Also, metallocene-catalyzed 10 polyolefins [can] may be used as the polymer component P1 The fiber polymer components P1 and P2 [can] may and/or P2. be spin-dyed, white-pigmented, or provided with agents that give the fiber polymer components hydrophilic or hydrophobic properties or reduced wettability with alcohol, other organic 15 fluids, fats, or oils. Furthermore, the fiber polymer components [can] may be mixed with anti-static agents or antimicrobial substances.

According to the present invention, in addition to the split 20 fibers, at least a second fiber component is also used, which is composed in part or by 100% of a polymer soluble in hot water, where the portion of the nonwoven fabric soluble in hot water is 10 to 70 wt.-%. In the sense of the invention, solubility of the fibers in hot water is understood to mean a 25 solubility in water under the conditions of high-pressure water jet treatment of less than 5%, and a solubility of at least 95% in water with a temperature of approximately 98 °C, i.e., in pressure containers at temperatures above 100 °C. Fibers soluble in hot water, in the sense of the invention, 30 are also fibers that do not go into solution until they are treated with pressure in an autoclave, or swell up under these conditions to such an extent that they are removed by at least 95% from the nonwoven fabric when subjected to a washing procedure. [Preferred fibers] Fibers that are soluble in hot 35

water [are] <u>may include</u> fibers made of polyvinyl alcohol or poly- $\epsilon$ -caprolactone.

The nonwoven fabric [can] <u>may</u> contain other fibers, in addition to the splittable fibers and the fibers soluble in hot water, but nonwoven fibers made of the two fiber types stated are [preferred] <u>possible</u>. The weight ratio of the split fibers and fibers soluble in hot water is 90:10 to 30:70, [preferably] <u>e.g.</u>, 70:30 to 50:50.

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The fiber soluble in hot water [can] may be present in weakly cross-linked form. Also, fibers that possess only a coating of a polymer soluble in hot water, i.e. fibers that have a core-mantle structure, [can] may be used as the fibers soluble in hot water. Furthermore, fibers with a side-by-side structure that are made up of different polymers, only one of which is soluble in hot water, are suitable. According to the present invention, the split fiber does not possess any coating that is soluble in hot water. Introduction of the fibers soluble in hot water [takes place] occurs statistically in accordance with their proportion, for example by carding or the air-laid process or deposition on a slanted screen in accordance with the Fourdrinier method. In the case of split fiber endless filaments, fibers that are soluble in hot water are blown in at the side, using an air stream, into the endless filaments that exit from the spinning dies and are quenched and stretched by a directed air stream before being deposited on a screen belt, or the addition [takes place] occurs from a separate spinning beam. The split fibers and fibers soluble in hot water that are used [preferably] may have a wavy structure. The fibers deposited to form a nonwoven sheet are transferred to a water removal screen and subjected to high-pressure water-jet treatment. In a first stage, the fibers are merely intertwined, using a low water-jet pressure, to form a nonwoven fabric highly resistant to tearing. Subsequently, splitting of the split fibers to form microfibers with a titer between 0.05 to 1.0 dtex, [preferably] e.g., 0.1 to 0.3 dtex, [takes place] occurs using one or more high-pressure water-jet beams. The fineness of the released microfibers [can] may be adjusted by the titer of the split fibers in the unsplit state and the number of segments. To prevent water-jet alleys in the nonwoven fabric, at least the last water-jet beams are put into oscillating motion perpendicular to the machine transport direction. Furthermore, to reduce alley formation, screens with a closer mesh [can] may be used, which cause reflection and scattering of the incident water jets, and thereby cause the water-jet alleys to be made less distinct. Nonwoven fabrics with a surface weight of 80 to 1,000  $g/m^2$ , [preferably] e.g., 100 to 500 g/m<sup>2</sup>, are produced using the process according to the present invention. [Preferably, the] The nonwoven fabric [is] may be mechanically needle-punched, in addition, before the The process according to the present hydrodynamic treatment. invention is conducted [in such a way] **so** that after splitting to form microfibers, a maximum of 3 to 5 wt.-% of the fibers soluble in hot water is dissolved out of the nonwoven fabric by the water-jet needle-punching and splitting process. consolidated nonwoven fabric that is obtained is impregnated, in [known] a conventional manner, with an aqueous binder dispersion, using the dry-in-wet application method. application [can take place] may occur by brushing, slop padding from one side, or full-bath impregnation in a Foulard. Application of the binder to one side [can] may be promoted by applying a vacuum on the opposite side of the nonwoven fabric. The binder application [takes place] occurs at a ratio of 25:75 to 75:25 wt.-%, [preferably] e.g., 35:65 to 65:35 wt.-%, in relation to the prefinished nonwoven fiber fabric, i.e., before the fibers soluble in hot water are dissolved out. Polymers that contain self-cross-linking reactive groups in the polymer, or polymers mixed with cross-linking agents, are

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used as binders. In the selection of the polymer dispersions and cross-linking agents, care [must] may be taken to ensure that the reactive groups in the fibers soluble in hot water either remain non-cross-linked or that the degree of cross-linking is kept so low that the water solubility is retained, to remove the portion according to the present invention. Binders that are used in the sense of the invention are polymer dispersions made of polyurethane, nitrile-butadiene rubber and/or styrene-butadiene rubber. Binders that smear when buffed or ground with sandpaper or on ceramic rollers are not binders in the sense of the invention. The binder [can have known] may include conventional substances, such as inorganic white pigments, colored -pigments, agents to improve the feel, such as silicones, cellulose dust, optical brighteners, anti-static agents, bacteriostatics added to them. After the binder application, the nonwoven fabric is dried[; if]. If necessary, this is preceded by thermocoagulation and cross-linking or vulcanization. Subsequently, [it is advantageous if] the synthetic leather obtained [is] may be buffed and pre-ground. Removal of the fibers soluble in hot water [takes place] occurs either without pressure, under hot-water washing conditions, or in an autoclave, at bath temperatures above 100 In this [way] manenr, the fiber soluble in hot water is removed from the microfiber nonwoven fabric. [Preferably, dissolving] Dissolving out the fiber soluble in hot water [can] may also be combined with an exhaust-dyeing process, if high dyeing temperatures are being used in any case, [particularly] e.g., in an autoclave. Using the process according to the present invention, synthetic leathers that are extremely soft and firm, with excellent haptic properties, are obtained. To improve the microfiber nap, additional subsequent treatment steps, such as application of a finish to improve the feel, or fine-grinding of the surfaces, [preferably take place] may occur.

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## Example

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A fiber layer is produced from 80 parts by weight of a polyester-polyamide split fiber with a titer of 2.2 dtex and a fiber length of 51 mm as well as 20 parts by weight of a polyvinyl alcohol fiber with a titer of 1.4 dtex and a fiber length of 38 mm, and this layer is needle-punched intensively to consolidate it. The nonwoven fabric obtained in this [way] manner is subjected to high-pressure water-jet treatment, during which approximately 90 % of the polyester-polyamide fibers are split into microfibers. Subsequently, the nonwoven fabric is impregnated with a binder, where this is composed of aqueous dispersions that contain 70 parts by weight polyurethane, 20 parts by weight polyvinyl alcohol, 5 parts by weight colored pigments, as well as fillers and agents to improve the feel as solid components, for the remainder. After the impregnated nonwoven fabric is dried, the polyvinyl alcohol fibers are removed from the nonwoven fabric by more than 95 wt.-% by treatment in a hot-water washing cycle. synthetic leather obtained has a very round feel and [can] may be processed to produce a material with a nubuck appearance by subsequent grinding.

## [Abstract

#### ] ABSTRACT

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[The invention relates to a method] A method is for producing a synthetic leather made up of a nonwoven fabric that contains microfibers. [According to the present invention, production takes place] Production occurs in that thermoplastic microfibers with a titer of 0.05 to 1.0 dtex and fibers soluble in hot water, with a titer of 4 to 6 dtex, are processed, in a weight ratio of 90:10 to 30:70, to form a nonwoven fabric with a surface weight of 80 to 1,000 g/m², and impregnated with an aqueous polymer dispersion of a viscoelastic substance in a weight ratio of 25:75 to 75:25 of the nonwoven fabric to the viscoelastic substance, fixation of the viscoelastic substance [takes place] occurs by cross-linking or vulcanization, and subsequently the fibers soluble in hot water are extracted from the nonwoven fabric.

[22750/534]

#### METHOD FOR PRODUCING A SYNTHETIC LEATHER

Specification

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The invention relates to a method for producing a synthetic leather made up of a nonwoven fabric that contains microfibers.

Synthetic leathers based on nonwoven fabrics are built up almost exclusively of microfibers at present. It has been shown that homogeneous microfibers as such cannot be processed on carding machines, or can be processed only at unjustifiable, extremely low production speeds. Therefore preferably multi-component fibers such as matrix-fibril fibers or island-in-sea type fibers are used, or others with a different distribution of the preferably two-fiber components, with a fiber titer such that they can be carded without loss The cross-sections of such fibers have an orange structure or a pie structure or hollow pie structure, for Such multi-component fibers (conjugate fibers, multiconstituent fibers) can be made up of at least two, but preferably up to approximately 18 segments. The individual fiber segments of the usually two polymers alternate with one another, so that after each segment, fiber border surfaces, such as polyethylene terephthalate/polyamide 6, are formed. The separation of these multi-component fibers to yield isolated, ultrafine microfibers is done using different methods. For example, one of the two fiber components is dissolved out, using organic solvents, so that the other fiber component, which is insoluble in the organic solvent, remains behind as a microfiber. This method is complicated, not good for the environment, and connected with a high level of material loss as well as the accumulation of solvent that contains polymer, where treatment of the used solvent takes place either by solvent recycling or energy utilization.

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An environmentally friendly separation of the bi-component fibers, which is preferred at present, takes place by splitting the fibers using high-pressure water jets. The bicomponent split fibers are either composed of thermoplastics that are greatly different in terms of their chemistry, which do not possess any high adhesion forces bonding them to one another at their border surfaces, or which have been mixed with dehesive additives, i.e. additives that reduce the adhesion forces, if the fiber polymers are similar. A synthetic leather with a soft feel is known from the document JP 05078986, which contains a nonwoven fabric layer of meltblown polyethylene terephthalate microfibers with a diameter of 0.1 to 0.6  $\mu m$  on at least one side. The softness is achieved in that the nonwoven fabric is coated with a dressing of polyvinyl alcohol that is soluble in cold water, before being impregnated with polyurethane from organic solvents such as dimethyl formamide. After impregnation and coagulation of the polyurethane solution with water (so-called migration method), and the subsequent wash cycles for the purpose of removing the organic solvent, the polyvinyl alcohol is removed from the nonwoven fabric again, at the same time. Subsequent treatment of the synthetic leather obtained takes place in known manner, by grinding, dyeing, and brushing. A 4,390,566 describes the production of a synthetic leather in which split microfibers are used, among other things. microfiber nonwoven fabric is impregnated with a water-soluble dressing solution that is referred to as a temporary filler, before the binder is applied, and after the binder application has consolidated, this solution is washed out again. Polyvinyl alcohol (PVA), poly-ε-caprolactone, carboxymethyl cellulose (CMC) or starch are used as temporary water-soluble fillers.

The invention has set itself the task of indicating a process that permits the production of a very soft synthetic leather with improved properties. Another task of the invention is to

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make production more cost-effective and better for the environment.

This task is accomplished, according to the present invention, by a process in which thermoplastic microfibers with a titer of 0.05 to 1.0 dtex and fibers soluble in hot water, with a titer of 4 to 6 dtex, are processed, in a weight ratio of 90:10 to 30:70, to form a nonwoven fabric with a surface weight of 80 to 1,000 g/m², and an aqueous polymer dispersion of a viscoelastic substance is applied and consolidated in a weight ratio of 25:75 to 75:25 of the nonwoven fabric to the viscoelastic substance, where subsequently extraction of the fibers soluble in hot water takes place.

Preferably, the process according to the present invention is one in which the titer of the thermoplastic fibers is 0.1 to 0.3 dtex, the weight ratio of the microfibers to the fibers soluble in hot water is 70:30 to 50:50 wt.-%, the surface weight of the nonwoven fabric is 100 to 500 g/m², and the ratio of the nonwoven fabric to the viscoelastic substance before removal of the fibers that are soluble in hot water is 35:65 to 65:35 wt.-%.

It is especially preferred according to the process according to the present invention that the thermoplastic fibers are split fibers.

Furthermore, it is preferred that the split fibers are composed of polyethylene terephthalate/polyamide 6, polyethylene terephthalate/polyamide 6.6, polyethylene terephthalate/polypropylene, or polyethylene terephthalate/polyethylene.

Preferably, fibers that are soluble in hot water that are made of polyvinyl alcohol, poly- $\epsilon$ -caprolactone, carboxymethyl cellulose, or starch, are used in the process according to the present invention.

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Consolidation and splitting of the nonwoven fabric of fibers preferably takes place using high-pressure water jets.

Furthermore, it is preferred that an aqueous polymer dispersion of polyurethane, nitrile-butadiene rubber, or styrene-butadiene rubber is used as the binder.

Preferably it is provided, according to the process according to the present invention, that fillers such as pigments, hydrophobization or hydrophilization agents, agents to reduce wettability with alcohols, fats and oils, anti-static agents and/or antimicrobial substances are added to the thermoplastic fibers.

In an advantageous further development of the process, it is provided that subsequent treatment takes place by buffing, grinding, or polishing with emery.

It is especially preferred according to the process according to the present invention that dissolving out the fibers that are soluble in hot water takes place at the same time with exhaust dyeing, particularly in an autoclave.

The process according to the present invention is not only simple, i.e. it makes do with only a few process steps, it also, at the same time, permits more cost-effective and environmentally friendly production of the synthetic leather.

Using the process according to the present invention, there is no need to use organic solvents to release the microfibers, or to apply the binder coagulation.

The production of a synthetic leather, according to the present invention, takes place in that a fiber sheet is produced from endless fibers, staple fibers, or short-cut fibers, using the known fiber laying techniques. This fiber sheet is made up of at least two fiber components, where at

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least one of the fiber components is a bi-component fiber that can be split using high-pressure water jets. Such split fibers are made up of at least two thermoplastic polymer components, P1 and P2, which are arranged in segments around the fiber axis, in alternating sequence. In this connection, both centric and eccentric fiber axis arrangements are The number of segments lies between 2 and 30, possible. preferably, however, between 4 and 24. The total titer of these so-called pie fibers lies between 0.8 and 5.0, preferably between 1.0 and 3.3 dtex. According to the present invention, other geometric arrangements of the fiber polymers P1 and P2 are also possible, with the proviso that the fibers are split up into microfibers by at least 80% under strong mechanical or hydrodynamic forces, such as treatment with high-pressure water jets. Preferably, the polymer pairs P1 and P2 are ones whose common border surfaces do not exert any strong adhesion forces on one another. Known P1/P2 pairs are, for example, polyethylene terephthalate/polyamide 6, polyethylene terephthalate/polyamide 6.6, polyethylene terephthalate/polypropylene, and polyethylene terephthalate/polyethylene. For P1/P2 pairs that are closely related in terms of chemistry, such as polypropylene and polyethylene or their copolymers, it is known to provide them with parting agents at their border surfaces, which ensure splittability. Also, metallocene-catalyzed polyolefins can be used as the polymer component P1 and/or P2. The fiber polymer components P1 and P2 can be spin-dyed, white-pigmented, or provided with agents that give the fiber polymer components hydrophilic or hydrophobic properties or reduced wettability with alcohol, other organic fluids, fats, or oils. Furthermore, the fiber polymer components can be mixed with anti-static agents or antimicrobial substances.

According to the present invention, in addition to the split fibers, at least a second fiber component is also used, which is composed in part or by 100% of a polymer soluble in hot water, where the portion of the nonwoven fabric soluble in hot

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water is 10 to 70 wt.-%. In the sense of the invention, solubility of the fibers in hot water is understood to mean a solubility in water under the conditions of high-pressure water jet treatment of less than 5%, and a solubility of at least 95% in water with a temperature of approximately 98 °C, i.e. in pressure containers at temperatures above 100 °C. Fibers soluble in hot water, in the sense of the invention, are also fibers that do not go into solution until they are treated with pressure in an autoclave, or swell up under these conditions to such an extent that they are removed by at least 95% from the nonwoven fabric when subjected to a washing procedure. Preferred fibers that are soluble in hot water are fibers made of polyvinyl alcohol or poly- $\epsilon$ -caprolactone.

The nonwoven fabric can contain other fibers, in addition to the splittable fibers and the fibers soluble in hot water, but nonwoven fibers made of the two fiber types stated are preferred. The weight ratio of the split fibers and fibers soluble in hot water is 90:10 to 30:70, preferably 70:30 to 50:50.

The fiber soluble in hot water can be present in weakly cross-Also, fibers that possess only a coating of a linked form. polymer soluble in hot water, i.e. fibers that have a coremantle structure, can be used as the fibers soluble in hot water. Furthermore, fibers with a side-by-side structure that are made up of different polymers, only one of which is soluble in hot water, are suitable. According to the present invention, the split fiber does not possess any coating that is soluble in hot water. Introduction of the fibers soluble in hot water takes place statistically in accordance with their proportion, for example by carding or the air-laid process or deposition on a slanted screen in accordance with the Fourdrinier method. In the case of split fiber endless filaments, fibers that are soluble in hot water are blown in at the side, using an air stream, into the endless filaments that exit from the spinning dies and are quenched and

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stretched by a directed air stream before being deposited on a screen belt, or the addition takes place from a separate spinning beam. The split fibers and fibers soluble in hot water that are used preferably have a wavy structure. fibers deposited to form a nonwoven sheet are transferred to a water removal screen and subjected to high-pressure water-jet In a first stage, the fibers are merely treatment. intertwined, using a low water-jet pressure, to form a nonwoven fabric highly resistant to tearing. Subsequently, splitting of the split fibers to form microfibers with a titer between 0.05 to 1.0 dtex, preferably 0.1 to 0.3 dtex, takes place using one or more high-pressure water-jet beams. fineness of the released microfibers can be adjusted by the titer of the split fibers in the unsplit state and the number of segments. To prevent water-jet alleys in the nonwoven fabric, at least the last water-jet beams are put into oscillating motion perpendicular to the machine transport direction. Furthermore, to reduce alley formation, screens with a closer mesh can be used, which cause reflection and scattering of the incident water jets, and thereby cause the water-jet alleys to be made less distinct. Nonwoven fabrics with a surface weight of 80 to 1,000  $g/m^2$ , preferably 100 to 500  $g/m^2$ , are produced using the process according to the present invention. Preferably, the nonwoven fabric is mechanically needle-punched, in addition, before the hydrodynamic treatment. The process according to the present invention is conducted in such a way that after splitting to form microfibers, a maximum of 3 to 5 wt.-% of the fibers soluble in hot water is dissolved out of the nonwoven fabric by the water-jet needle-punching and splitting process. consolidated nonwoven fabric that is obtained is impregnated, in known manner, with an aqueous binder dispersion, using the dry-in-wet application method. The application can take place by brushing, slop padding from one side, or full-bath impregnation in a Foulard. Application of the binder to one side can be promoted by applying a vacuum on the opposite side of the nonwoven fabric. The binder application takes place at

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a ratio of 25:75 to 75:25 wt.-%, preferably 35:65 to 65:35 wt.-%, in relation to the prefinished nonwoven fiber fabric, i.e. before the fibers soluble in hot water are dissolved out. Polymers that contain self-cross-linking reactive groups in the polymer, or polymers mixed with cross-linking agents, are used as binders. In the selection of the polymer dispersions and cross-linking agents, care must be taken to ensure that the reactive groups in the fibers soluble in hot water either remain non-cross-linked or that the degree of cross-linking is kept so low that the water solubility is retained, to remove the portion according to the present invention. Binders that are used in the sense of the invention are polymer dispersions made of polyurethane, nitrile-butadiene rubber and/or styrenebutadiene rubber. Binders that smear when buffed or ground with sandpaper or on ceramic rollers are not binders in the The binder can have known substances, sense of the invention. such as inorganic white pigments, colored pigments, agents to improve the feel, such as silicones, cellulose dust, optical brighteners, anti-static agents, bacteriostatics added to them. After the binder application, the nonwoven fabric is dried; if necessary, this is preceded by thermocoagulation and cross-linking or vulcanization. Subsequently, it is advantageous if the synthetic leather obtained is buffed and pre-ground. Removal of the fibers soluble in hot water takes place either without pressure, under hot-water washing conditions, or in an autoclave, at bath temperatures above 100 In this way, the fiber soluble in hot water is removed from the microfiber nonwoven fabric. Preferably, dissolving out the fiber soluble in hot water can also be combined with an exhaust-dyeing process, if high dyeing temperatures are being used in any case, particularly in an autoclave. the process according to the present invention, synthetic leathers that are extremely soft and firm, with excellent haptic properties, are obtained. To improve the microfiber nap, additional subsequent treatment steps, such as application of a finish to improve the feel, or fine-grinding of the surfaces, preferably take place.

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## Example

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A fiber layer is produced from 80 parts by weight of a polyester-polyamide split fiber with a titer of 2.2 dtex and a fiber length of 51 mm as well as 20 parts by weight of a polyvinyl alcohol fiber with a titer of 1.4 dtex and a fiber length of 38 mm, and this layer is needle-punched intensively to consolidate it. The nonwoven fabric obtained in this way is subjected to high-pressure water-jet treatment, during which approximately 90 % of the polyester-polyamide fibers are split into microfibers. Subsequently, the nonwoven fabric is impregnated with a binder, where this is composed of aqueous dispersions that contain 70 parts by weight polyurethane, 20 parts by weight polyvinyl alcohol, 5 parts by weight colored pigments, as well as fillers and agents to improve the feel as solid components, for the remainder. After the impregnated nonwoven fabric is dried, the polyvinyl alcohol fibers are removed from the nonwoven fabric by more than 95 wt.-% by treatment in a hot-water washing cycle. The synthetic leather obtained has a very round feel and can be processed to produce a material with a nubuck appearance by subsequent grinding.

## What is claimed is:

- 1. A method for producing a synthetic leather made up of a nonwoven fabric that contains microfibers, wherein thermoplastic microfibers with a titer of 0.05 to 1.0 dtex and fibers soluble in hot water, with a titer of 4 to 6 dtex, are processed, in a weight ratio of 90:10 to 30:70, to form a nonwoven fabric with a surface weight of 80 to 1,000 g/m², and an aqueous polymer dispersion of a viscoelastic substance is applied and consolidated in a weight ratio of 25:75 to 75:25 of the nonwoven fabric to the viscoelastic substance, where subsequently extraction of the fibers soluble in hot water takes place.
- 2. The method according to Claim 1, wherein the titer of the thermoplastic fibers is 0.1 to 0.3 dtex, the weight ratio of the microfibers to the fibers soluble in hot water is 70:30 to 50:50 wt.-%, the surface weight of the nonwoven fabric is 100 to 500 g/m², and the ratio of the nonwoven fabric to the viscoelastic substance before removal of the fibers that are soluble in hot water is 35:65 to 65:35 wt.-%.
- 3. The method according to Claim 1 or 2, wherein the thermoplastic fibers are split fibers.
- 4. The method according to Claim 3, wherein the split fibers are composed of polyethylene terephthalate/polyamide 6, polyethylene terephthalate/polyamide 6.6, polyethylene terephthalate/polypropylene, or polyethylene terephthalate/polyethylene.
- 5. The method according to Claim 1 or 2, wherein fibers made of polyvinyl alcohol, poly- $\epsilon$ -caprolactone, carboxymethyl cellulose, or starch are used as the fibers soluble in hot water.

- 6. The method according to one or more of Claims 1 to 5, wherein consolidation and splitting of the nonwoven fabric takes place using high-pressure water jets.
- 7. The method according to one of Claims 1 to 6, wherein an aqueous polymer dispersion of polyurethane, nitrile-butadiene rubber, or styrene-butadiene rubber is used as the binder.
- 8. The method according to Claim 3 or 4, wherein fillers such as pigments, hydrophobization or hydrophilization agents, agents to reduce wettability with alcohols, fats and oils, anti-static agents and/or antimicrobial substances are added to the thermoplastic fibers.
- 9. The method according to one or more of Claims 1 to 8, wherein subsequent treatment takes place by buffing, grinding, or polishing with emery.
- 10. The method according to one or more of Claims 1 to 9, wherein dissolving out the fibers that are soluble in hot water takes place at the same time with exhaust dyeing, particularly in an autoclave.

#### Abstract

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The invention relates to a method for producing a synthetic leather made up of a nonwoven fabric that contains microfibers. According to the present invention, production takes place in that thermoplastic microfibers with a titer of 0.05 to 1.0 dtex and fibers soluble in hot water, with a titer of 4 to 6 dtex, are processed, in a weight ratio of 90:10 to 30:70, to form a nonwoven fabric with a surface weight of 80 to 1,000 g/m², and impregnated with an aqueous polymer dispersion of a viscoelastic substance in a weight ratio of 25:75 to 75:25 of the nonwoven fabric to the viscoelastic substance, fixation of the viscoelastic substance takes place by cross-linking or vulcanization, and subsequently the fibers soluble in hot water are extracted from the nonwoven fabric.



#### DECLARATION AND POWER OF ATTORNEY FOR NATIONAL STAGE OF PCT\_PATENT APPLICATION

As a below-named inventor, I hereby declare that:

Michael HOFSAESS

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **MEASURING INSTRUMENT AND METHOD FOR DETECTING A FORCE** the specification of which was filed as PCT International Application number PCT/DE 01/00591 on February 16, 2001.

I hereby state that I believe the named inventor or inventors in this Declaration to be the original and first inventor or inventors of the subject matter which is claimed and for which a patent is sought.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose all information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, Section 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) or Section 365 (b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate or PCT International application having a filing date before that of the application on which priority is claimed.

Prior	foreign	applica	tion(	s)
	10101011			

Priority claimed:

100 09 168.7 (Number)	_GERMANY(Country)	FEBRUARY 26, 20 (Date filed)	000 <u>X</u> Yes	No
(Number)	(Country)	(Date filed)	Yes	No

As a named inventor, I hereby appoint the following attorney to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statement may jeopardize the validity of the application or any patent issued thereon.



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